Reactive transport modelling for CO_2 injection with H_2 as a contaminant

Introduction

The carbon dioxide (CO_2) injection stream in CCS projects contains a variety of other gaseous species, with a wide range of concentrations from ppm (parts per million) to percentage levels. The composition of the CO_2 stream is dependent on the capture technology, fuel type, flue gas treatment and on the source of the CO_2. The CO_2 stream may be derived from thermal power production, refineries, biomass, cement plants, steel manufacturing, fertilizer plants as well as from hydrogen production (Mettz & Davidson, 2005) (M. Anheden, 2005) (Oosterkamp, 2008).

Several of these contaminants in the CO_2 injections stream are reactive with minerals in the subsurface, most notably H_2, H_2S, O_2, SO_x and NOx, causing precipitation and dissolution reactions or formation of toxic reaction products. H_2 can be present in concentrations up to 0.75 mol% for pre-combustion CO_2 streams (Mettz & Davidson, 2005) (M. Anheden, 2005) (Oosterkamp, 2008). Parallel efforts for H_2 storage have highlighted the risk of H_2S formation by reduction of pyrite by H_2 (Truche, et al., 2010). H_2S is toxic and can lead to sulfide stress cracking and corrosion in well materials (ISO, 2020). Low levels of H_2S may already be present in the CO_2 injection stream, which may further increase due to H_2-driven pyrite reduction. The CO_2 plume with hazardous reaction products may migrate to legacy wells or back to the injection well after shut in. The expected concentration ranges of H_2S may therefore impact well design and material selection, as well as health and safety precautions. It is therefore important to understand expected concentration ranges in the subsurface. This study aims to assess the impact of CO_2 injection and contaminants H_2 and H_2S, on the geochemical reactivity of the gas with the brine and minerals for CO_2 storage in a saline aquifer.

Background

Sulfide minerals, such as pyrite, may react with H_2, and thereby generate H_2S, see the net reaction below:

$$FeS_2 + H_2 + 2H^+ \rightleftarrows Fe^{2+} + 2H_2S$$

H_2S can be removed again by reacting with Fe^{2+} in the formation water, forming FeS (pyrrhotite). These reactions can be simulated using a geochemical database which defines the equilibrium state of reactions using an activity model. However, the H_2-induced reactions are slow at typical reservoir temperatures. Therefore, the database needs to be supplemented with kinetic rate equations and parameters for reactions that are out of thermodynamic equilibrium at the timescales and under the conditions of interest.

Therefore, N_2, CH_4, S and H_2 are redox-decoupled (see also Parkhurst and Appelo, 2013; Tremosa et al., 2023) and kinetically controlled or blocked, in case reactivity is negligible. For the H_2-induced pyrite dissolution reaction, a kinetic rate law was derived based upon the available data in literature from Truche et al. (2010) and formulated in a way that is suitable for RTM and added to the database.

Methods and input data

RTM is performed using MoReS-PHREEQC, Shell's inhouse RTM simulator (Wei, L., 2012), in combination with the Thermoddem database (Marty, 2015), adapted for geochemical modelling of H_2 in line with above discussion. After initialization of the model, RTM simulations were run in zero dimensions (0D), also commonly referred to as a batch model, to understand geochemical reaction pathways and conduct parameter sensitivities. This was followed up by modelling in a 1D and 2D radial geometry to understand geochemical reactions in combination with multiphase fluid flow behavior and dry-out effects. A 25-year injection period was modelled in which 0.75 Mt CO_2 injection per year is assumed. The 0D and 1D model were run up to 1000 years to assess the long-term effects of CO_2 injection.

The temperature of the reservoir is 60˚C and an average bottom hole injection temperature of 30˚C was used in the 1D and 2D model. The reservoir is a sandstone, dominated by quartz and with additionally feldspars, clay minerals and traces of pyrite. Since the precise amount of pyrite could not be quantified, a content of 0.2 vol% was assumed. The formation water is highly saline and dominated by sodium and chloride as the main ions in solution. The injection composition is shown in Table 1. An Equation of State (EOS) was derived using PVTsim with Peng Robinson 78 Peneloux.

Table 1. Simplified base case fluid composition used for RTM.

Compound	Mole fraction
CO_2	0.962495
C_1	0.020000
N_2	0.010000
H_2	0.007500
H_2S	0.000005

For the batch model, a water saturation of 0.6 is assumed and for the batch model and 1D model a porosity of 0.15 is used. The lateral extent of the 1D and 2D models is 5 km, with an inner grid block radius of 0.5 m (at the wellbore) increasing exponentially to a 500 m radius for the grid blocks at the periphery, and with an analytical infinite radial aquifer boundary condition applied to the outer radius. For the 2D radial model, the reservoir is divided into 38 layers with variable properties.

Results and discussion

The presence of H_2 as a contaminant in the CO_2 injection stream leads to H_2S generation due to pyrite reduction. This is a slow process, especially at the reservoir temperature of this study. Batch modelling results shows that, at best estimate input parameter values, after 50 years H_2S levels have increased from 5 to about 7 ppm only and up to 90 ppm after 1000 years. No precipitation of FeS (pyrrhotite) is predicted. Sensitivity runs show that a reduction of the temperature due to injection strongly reduces the rate of H_2S generation (Fig. 1). Also, a lower level of H_2 leads to a proportionally lower concentration of H_2S in the gas phase (i.e., the supercritical, CO_2-rich phase). The presence of Fe-containing minerals such as Fe-chlorite only has a limited impact on H_2S concentrations. That is because the additional Fe^{2+} is primarily scavenged by dissolved CO_2 to form siderite $FeCO_3$. The highest H_2S levels were observed if higher sulfide (H_2S) levels are present in the injected gas.

The main mineral reactions in the reservoir, upon injection of the CO_2, are the transition of albite, microcline and illite into quartz and kaolinite. The change in pyrite volume, controlled by the injected H_2, is small compared to these mineral transitions. The reaction with CO_2 leads to a drop in pH of 4.3, which recovers to pH 5.4 due to buffering reactions. The development of a dry-out front is predicted, extending to 10 m around the wellbore after 1 year and 50 m after 25 years. The main carbonate mineral forming is ankerite ($CaFe(CO_3)_2$). This leads to a mineralization of 2.7 vol% of the CO_2 after 1000 years, based upon 1D modelling results.

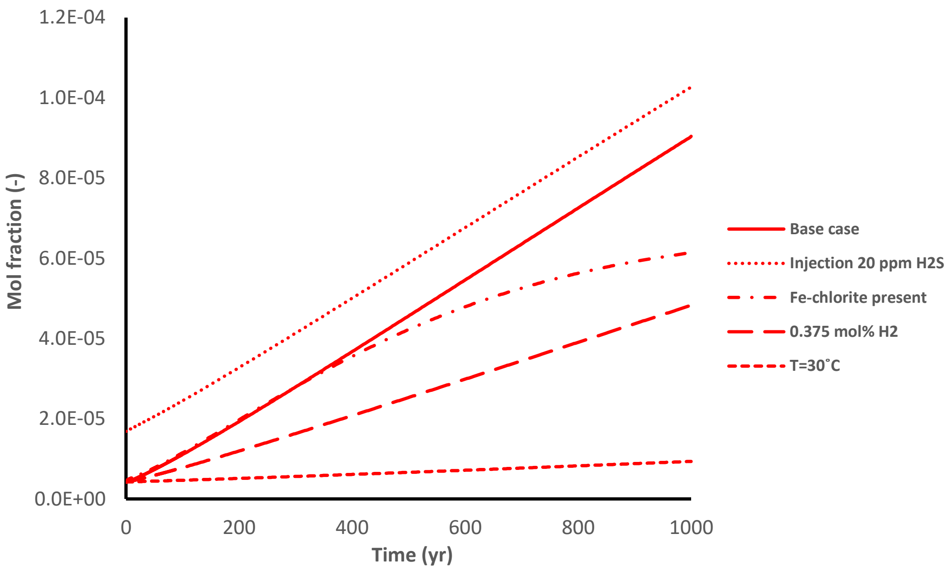

Figure 1. H_2S concentrations in gas (at subsurface conditions) for base case and sensitivity runs (0D simulations)

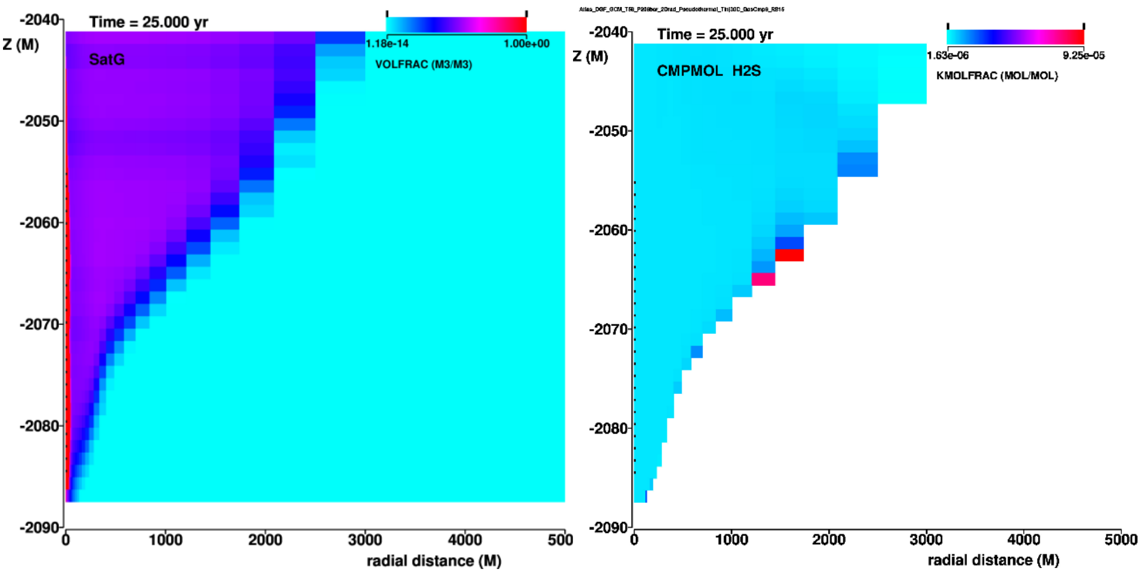

Figure 2. 2D RTM simulation results after 25 years, left: gas saturation, right: H_2S concentrations in the gas phase.

According to the 2D simulation results, the CO_2 plume moves sideways and, due to gravitational forces, upwards, causing the water to move downwards as well as sideways (Fig. 2). The H_2S is generated predominantly near the gas-waterfront (Fig. 2). During injection, this front is moving away from the injector. Therefore, during injection operations, the risk of elevated levels of H_2S near the wellbore is low. The development of the dry out region around the injector serves as an additional protection, because at zero water saturation all geochemical reactions come to a halt. In the figure, the H_2S concentration is primarily elevated in regions where the gas saturation is low, while in the gas plume the concentration increases only slightly. Increased risks may arise upon shut-in during a work-over and post closure. After shut-in, the water flow is reversed, where the gas continues to move upwards, and the water starts to move towards the well both from the side and from the bottom. The simulation results indicate that, most likely, there will not be elevated H_2S levels near wellbore within 25 years after shut in. Near the wellbore (within 10 m), the H_2S levels are expected to stay within 5-8 ppm mole in the gas phase. It should be mentioned that these results are based on the base case scenario only, and the impact of input parameter uncertainties on the conclusion were not investigated. As a general trend, in all regions where water and gas co-exist, H_2S concentrations are slowly increasing with time due to continued H_2-induced pyrite dissolution, until finally thermodynamic equilibrium is reached after about 2000 years with 205 ppm mole H_2S in the gas phase. This equilibrium level of H_2S may be reached quicker if microbial activity takes place. Considering the high affinity of microbes for H_2 which can tolerate high salinities (Dopffel et al., 2023), microbial conversion of H_2 and SO_4^{2-} to H_2S is possible, yet not considered in these simulations.

Conclusions and recommendations

Simulations predict that the presence of H_2 as a contaminant in the CO_2 injection stream leads to H_2S generation due to pyrite reduction. This is a slow process at the reservoir temperature in this case study (60˚C), leading to an increase from 5 to 7 ppm after 50 years (0D model). This level will not pose a significant risk or modification to material selection. The H_2S is predominantly generated at the front of the gas plume, hence during injection moving away from the wellbore. Therefore, the risk of elevated levels of H_2S near the wellbore during injection is expected to be low. Increased risks may arise upon shut-in during work overs. In addition, elevated H_2S levels are expected post closure and therefore should be considered in the abandonment strategy.

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